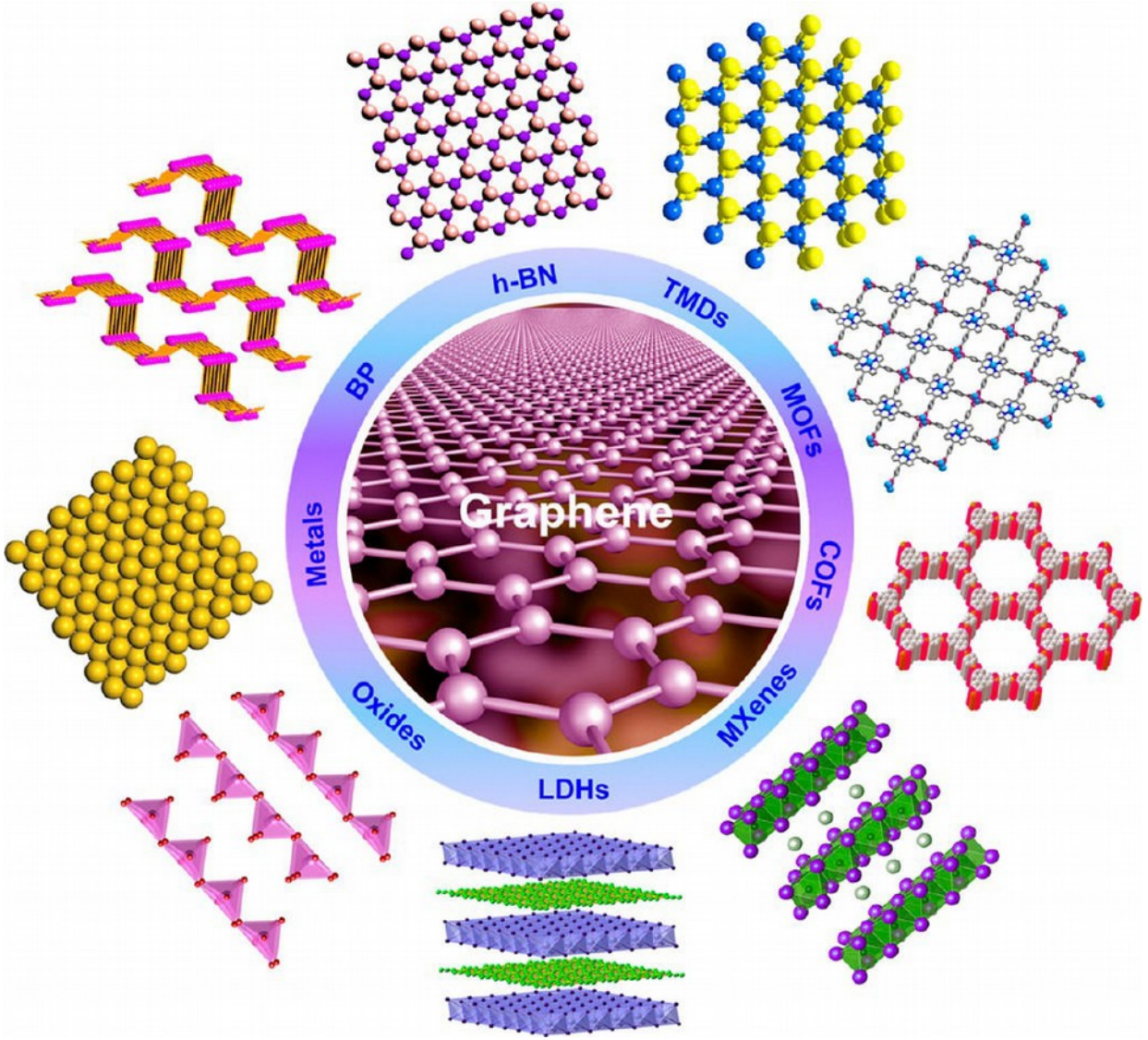
Prediction of Large-Gap Topological Insulator in functionalized Ordered Double Transition Metal MXene

Zhi-Quan Huang[1], Mei-Ling Xu[1], Gennevieve Macam[1], Chia-Hsiu Hsu[1] and Feng-Chuan Chuang[1]

1 Department of Physics, National Sun Yat-Sen University

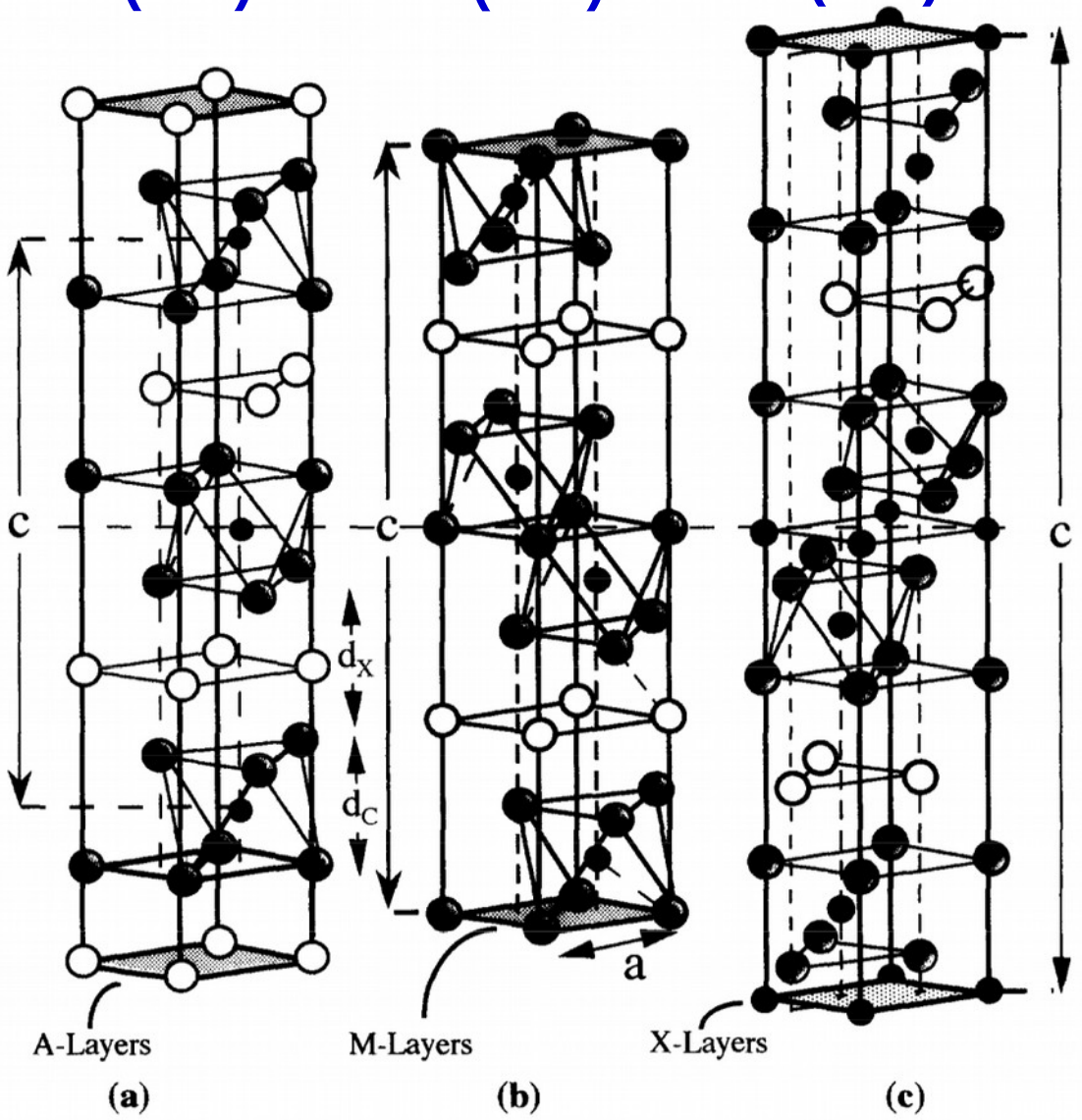
Different kinds of typical ultrathin 2D nanomaterials



H. Zhang, ACS Nano **9**, 9451 (2015).

$M_{n+1}AX_n$ Structure

M_2AX_1 (211) M_3AX_2 (312) M_4AX_3 (413)



$M_{n+1}AX_n$

n : 1, 2 or 3

M : early transition metal

A : A-group (mostly IIIA and IVA) element

X : C or N.

M. W. Barsoum, PROGRESS IN SOLID STATE CHEMISTRY **28**, 201 (2000).

Table of $M_{n+1}AX_n$

IIB	IIIA	IVA	VA	VIA
	Al Ti_2AlC, **4.11** (3.04,13.60) V_2AlC, **4.07** (3.1,13.83) Cr_2AlC, **5.24** (2.86,12.8) Nb_2AlC, **6.50**(3.10,13.8) Ta_2AlC, **11.82** (3.07,13.8) Ti_2AlN, **4.31** (2.989,13.614) Ti_3AlC_2, **4.5** (3.075,18.578) Ti_4AlN_3, **4.76** (2.988, 23.372)	**Si** Ti_3SiC_2 **4.52** (3.0665,17.671)	**P** V_2PC **5.38** (3.077,10.91) Nb_2PC **7.09** (3.28,11.5)	**S** Ti_2SC, **4.62** (3.216,11.22) Zr_2SC, **6.20** (3.40, 12.13) $Nb_2SC_{0.4}$, (3.27,11.4) Hf_2SC, (3.36, 11.99)
Zn	**Ga** Ti_2GaC, **5.53** (3.07, 13.52) V_2GaC, **6.39** (2.93, 12.84) Cr_2GaC, **6.81** (2.88, 12.61) Nb_2GaC, **7.73** (3.13, 13.56) Mo_2GaC, **8.79** (3.01, 13.18 Ta_2GaC, **13.05** (3.10, 13.57) Ti_2GaN, **5.75** (3.00, 13.3) Cr_2GaN, **6.82** (2.875, 12.77) V_2GaN, **5.94** (3.00, 13.3)	**Ge** Ti_2GeC, **5.68** (3.07, 12.93) V_2GeC, **6.49** (3.00, 12.25) Cr_2GeC, **6.88** (2.95, 12.08) Ti_3GeC_2, **5.55** (3.07, 17.76)	**As** V_2AsC **6.63** (3.11, 11.3) Nb_2AsC **8.025** (3.31, 11.9)	**Se**
Cd Ti_2CdC **9.71** (3.1, 14.41)	**In** Sc_2InC Ti_2InC, **6.2** (3.13, 14.06) Zr_2InC, **7.1** (3.34, 14.91) Nb_2InC, **8.3** (3.17,14.37) Hf_2InC, **11.57** (3.30,14.73) Ti_2InN, **6.54** (3.07,13.97) Zr_2InN, **7.53** (3.27,14.83)	**Sn** Ti_2SnC, **6.36** (3.163,13.679) Zr_2SnC, **7.16** (3.3576, 14.57) Nb_2SnC, **8.4** (3.241,13.802) Hf_2SnC, **11.8** (3.320,14.388) Hf_2SnN, **7.72** (3.31,14.3)	**Sb**	**Te**
	Tl Ti_2TlC, **8.63** (3.15,13.98) Zr_2TlC, **9.17** (3.36,14.78) Hf_2TlC **13.65** (3.32,14.62) Zr_2TlN, **9.60** (3.3,14.71)	**Pb** Ti_2PbC, **8.55** (3.20,13.81) Zr_2PbC, **9.2** 3.38,14.66 Hf_2PbC, **12.13** (3.55,14.46)	**Bi**	

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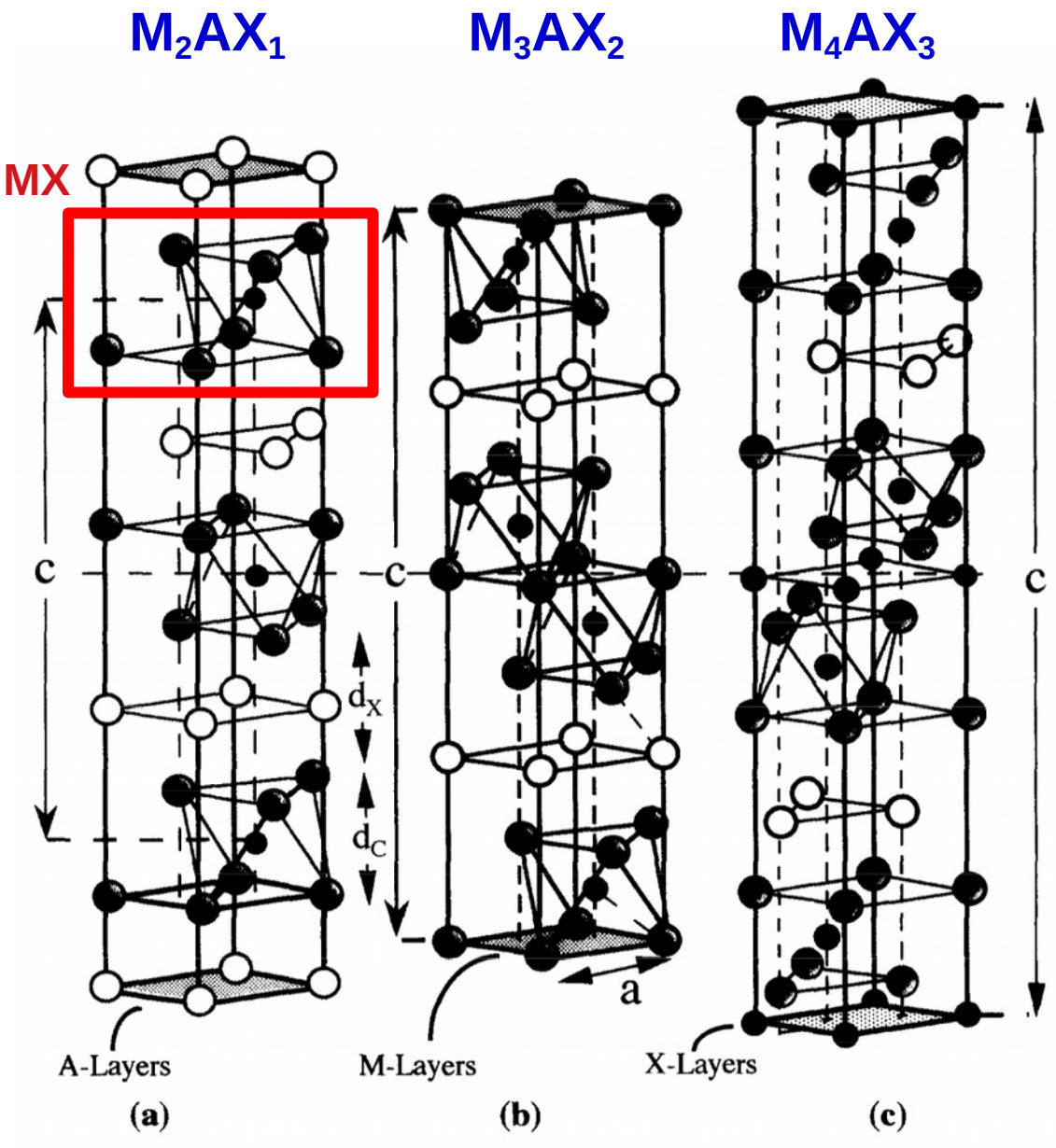
M. W. Barsoum, PROGRESS IN SOLID STATE CHEMISTRY **28**, 201 (2000).

$M_{n+1}AX_n$ Structure



$M_{n+1}AX_n$

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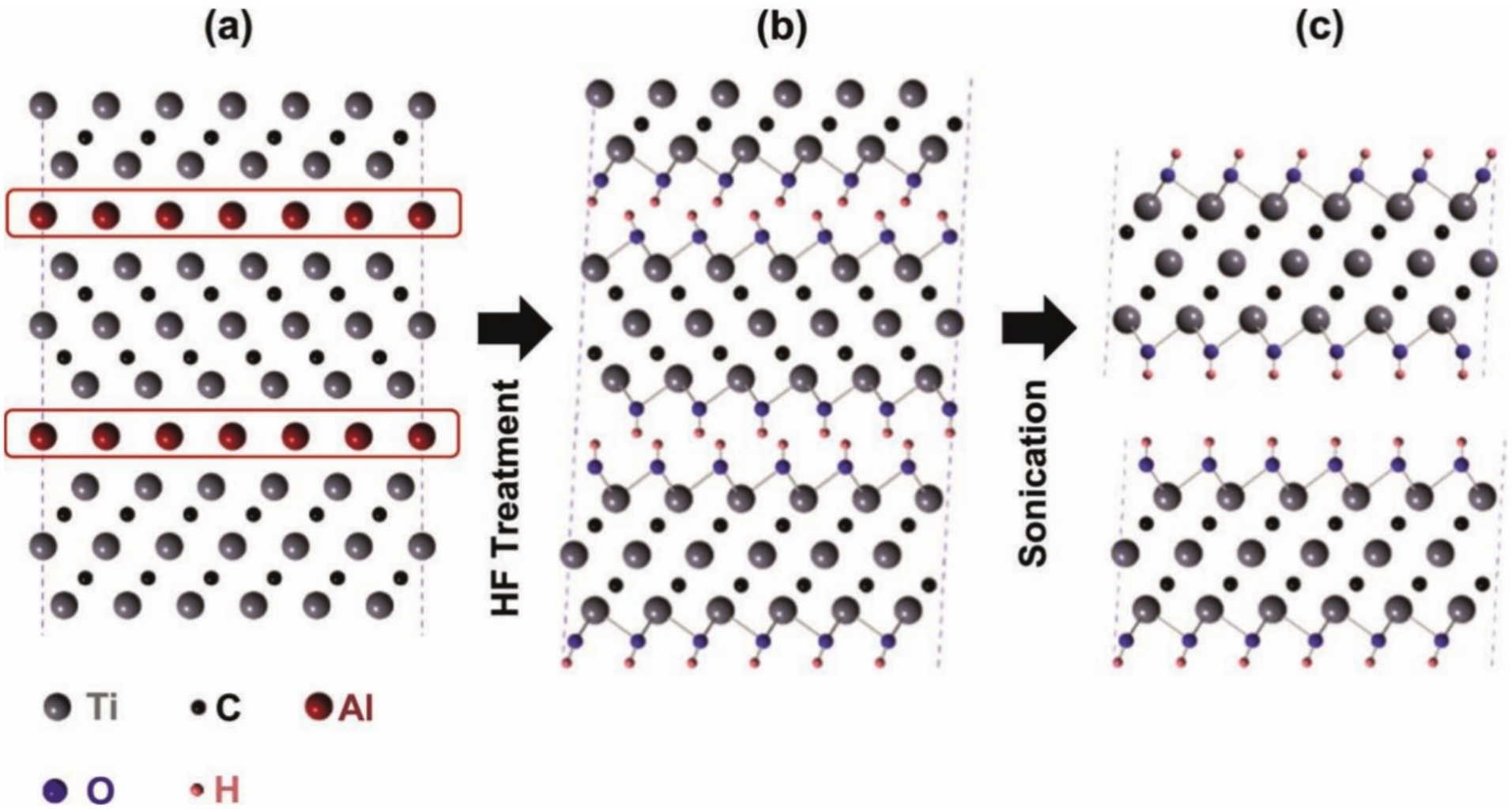
M. W. Barsoum, PROGRESS IN SOLID STATE CHEMISTRY **28**, 201 (2000).

Two-Dimensional Nanocrystals Produced by Exfoliation of Ti_3AlC_2

Ti_3AlC_2 structure

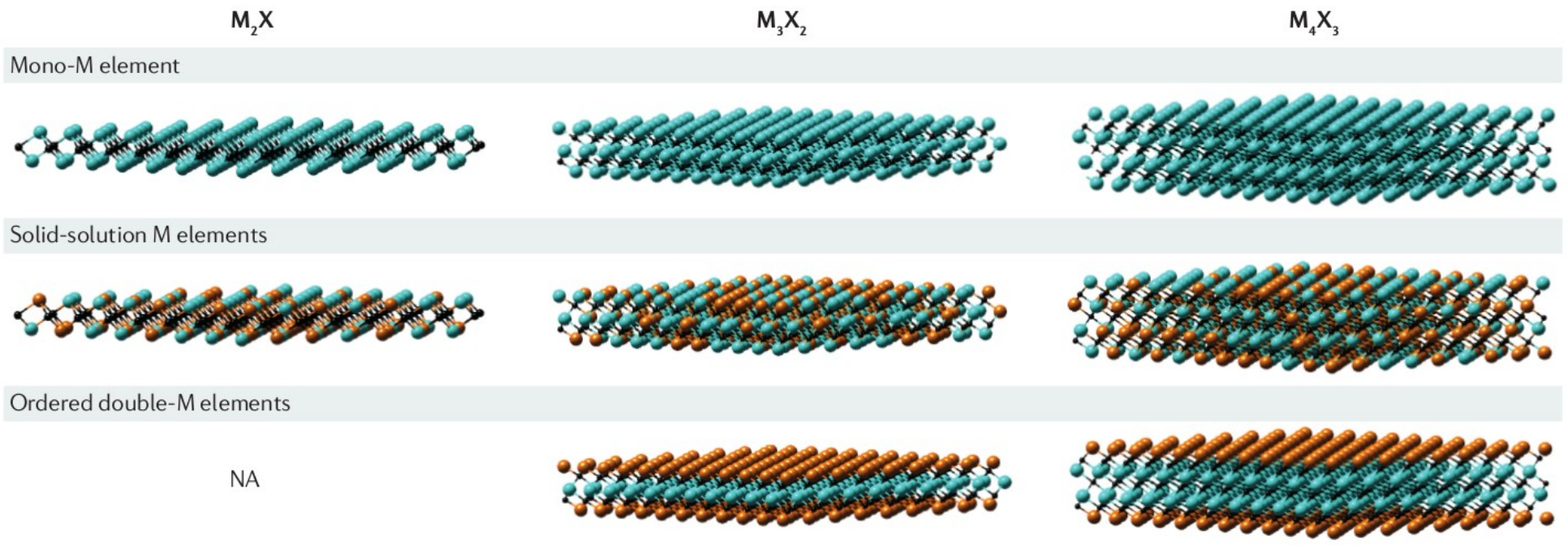
Al atoms replaced by OH

Breakage of the hydrogen bonds and separation



M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, and M. W. Barsoum, Advanced Materials **23**, 4248 (2011).

MXene Structure



$M_{n+1}X_nT_x$

n : 1, 2 or 3

M : early transition metal

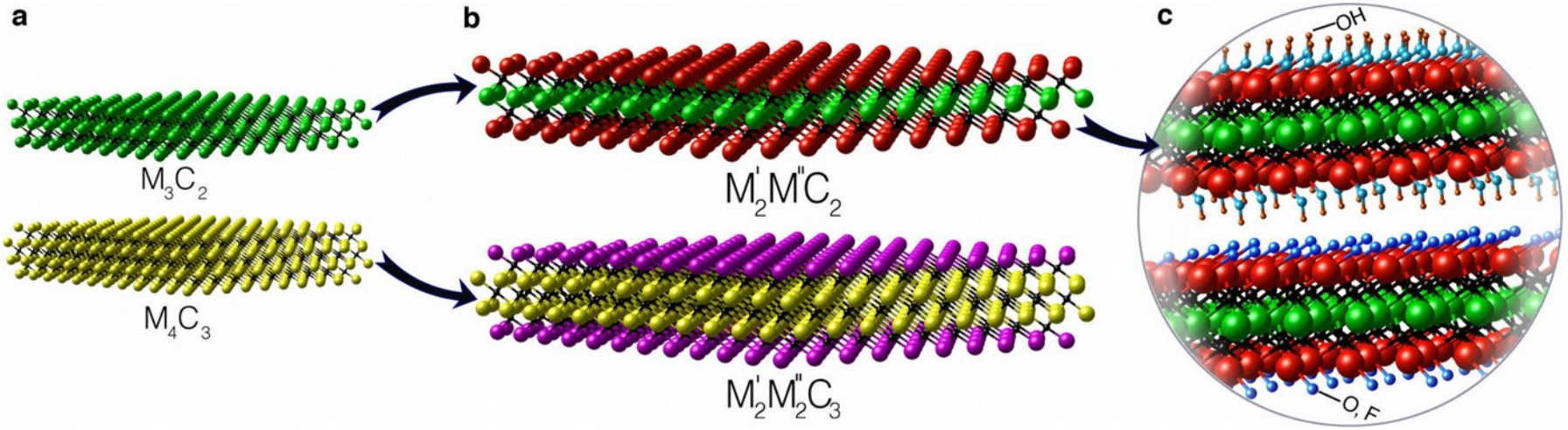
X : C or N

T : stands for the surface terminations (ex. H, O, F)

B. Anasori, M. R. Lukatskaya, and Y. Gogotsi, Nature Reviews Materials 2, 16098 (2017).

MXenes and Double Transition Metals MXenes

MXenes **Double Transition Metals MXenes**



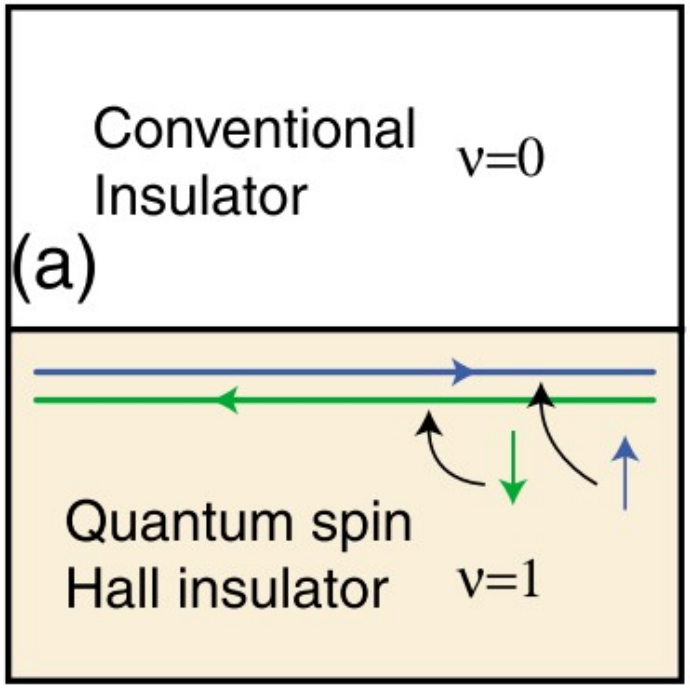
B. Anasori, Y. Xie, M. Beidaghi, J. Lu, B. C. Hosler, L. Hultman, P. R. C. Kent, Y. Gogotsi, and M. W. Barsoum, ACS Nano 9, 9507 (2015).

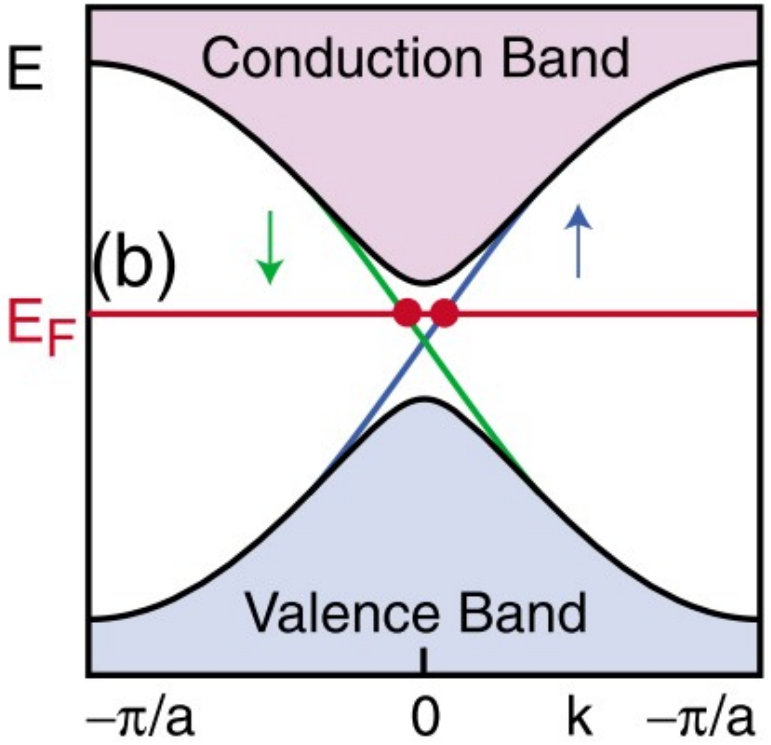
Sc_2C	Ti_2C	Ti_2N	Zr_2C	Ti_3C_2	Ti_3N_2	$Ti_3(C,N)_2$	Zr_3C_2	Ti_4N_3	V_4C_3	Nb_4C_3	Ta_4C_3
Zr_2N	Hf_2C	Hf_2N	V_2C	$(Ti,V)_3C_2$	$(Cr,V)_3C_2$	$(Ti_2Ta)C_2$	$(Ti_2Nb)C_2$	$(Ti,Nb)_4C_3$	$(Nb,Zr)_4C_3$	$(Ti_2Nb_2)C_3$	$(Ti_2Ta_2)C_3$
V_2N	Nb_2C	Ta_2C	Cr_2C	$(Cr_2V)C_2$	$(Mo_2V)C_2$	$(Cr_2Nb)C_2$	$(Cr_2Ta)C_2$	$(V_2Ti_2)C_3$	$(V_2Nb_2)C_3$	$(V_2Ta_2)C_3$	$(Nb_2Ta_2)C_3$
Cr_2N	Mo_2C	W_2C		$(Mo_2Ti)C_2$	$(Cr_2Ti)C_2$	$(Mo_2Nb)C_2$	$(Mo_2Ta)C_2$	$(Cr_2Ti_2)C_3$	$(Cr_2V_2)C_3$	$(Cr_2Nb_2)C_3$	$(Cr_2Ta_2)C_3$
$(Ti,V)_2C$	$(Ti,Nb)_2C$							$(Mo_2Ti_2)C_3$	$(Mo_2V_2)C_3$	$(Mo_2Nb_2)C_3$	$(Mo_2Ta_2)C_3$

Experimental Theoretical Ordered double-M Solid-solution M

B. Anasori, M. R. Lukatskaya, and Y. Gogotsi, Nature Reviews Materials 2, 16098 (2017).

(2D) Topological insulators





- ν does not change without closing the gap.
- Quantum spin Hall edge states

- Protected by time-reversal symmetry
- No backscattering

M.Z. Hasan and C.L. Kane, *Rev. Mod. Phys.* **82**, 3045 (2010)

Nano Lett. 16, 6584 (2016)

Large-Gap Quantum Spin Hall State in MXenes: *d*-Band Topological Order in a Triangular Lattice

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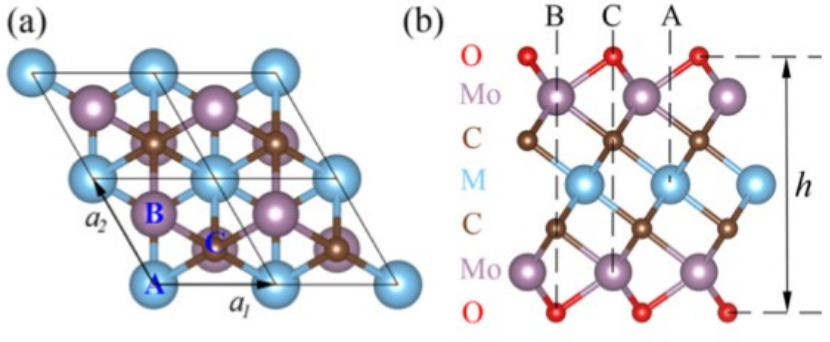


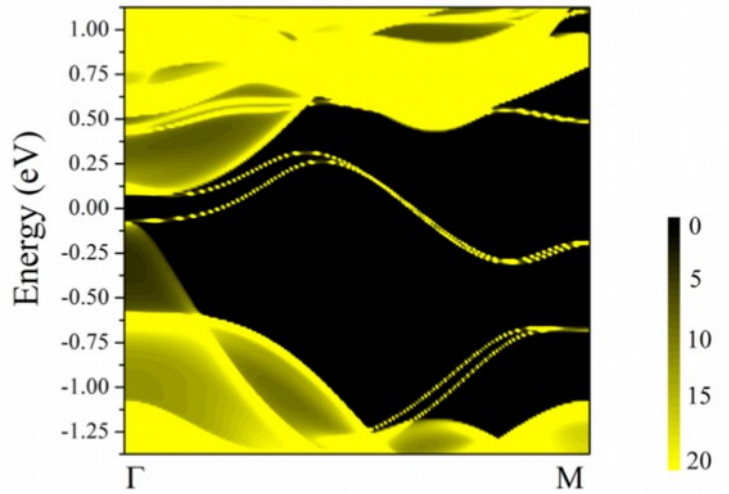
Figure 1. (a) Top view of the crystal structure of Mo_2MC_2 (M = Ti, Zr, or Hf) MXene displaying the hexagonal unit cell with Bravais lattice vectors a_1 and a_2. (b) Side view of the crystal structure of $Mo_2MC_2O_2$. h denotes the thickness of septuple atomic layers of $Mo_2MC_2O_2$.

Table 1. Lattice Constants (a), Thickness (h), Nontrivial Gaps at the Γ Point (E_Γ), Indirect Bulk Gaps (E_{bulk}), and Z_2 Topological Invariants for $Mo_2MC_2O_2$[a]

compound		$Mo_2TiC_2O_2$	$Mo_2ZrC_2O_2$	$Mo_2HfC_2O_2$
a (Å)		2.94	3.02	3.01
h (Å)		7.59	7.79	7.75
E_Γ (eV)	GGA	0.052	0.087	0.213
	HSE06	0.125	0.147	0.301
E_{bulk} (eV)	GGA	0.041	0.066	0.154
	HSE06	0.096	0.105	0.201
Z_2		1	1	1

[a]The values of E_Γ and E_{bulk} calculated by GGA and HSE06 are all shown for comparison.

$Mo_2HfC_2O_2$ on the zigzag edge



Phys. Rev. B **94**, 125152 (2016)

Topological insulators in the ordered double transition metals $M'_2M''C_2$ MXenes (M' = Mo, W; M'' = Ti, Zr, Hf)

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[2]*International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Ibaraki, Japan*
[3]*Computational Condensed Matter Physics Laboratory, RIKEN, Wako, Saitama 351-0198, Japan*
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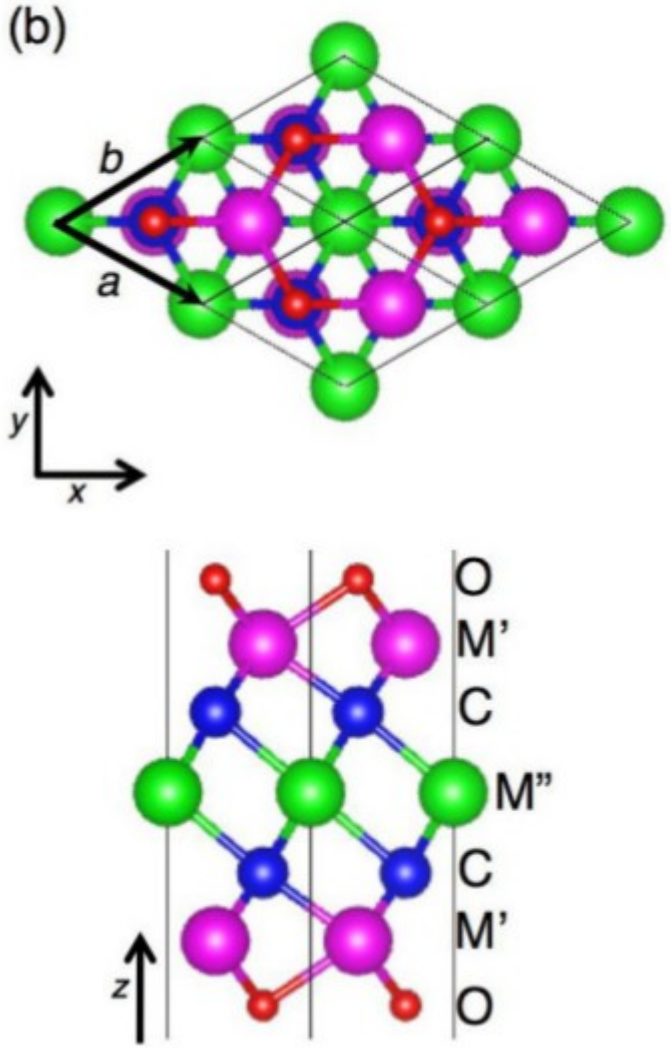
(Received 27 July 2016; revised manuscript received 7 September 2016; published 30 September 2016)



$M_2MC_2O_2$ (M = Mo, W; M = Ti, Zr, Hf) MXenes are TIs

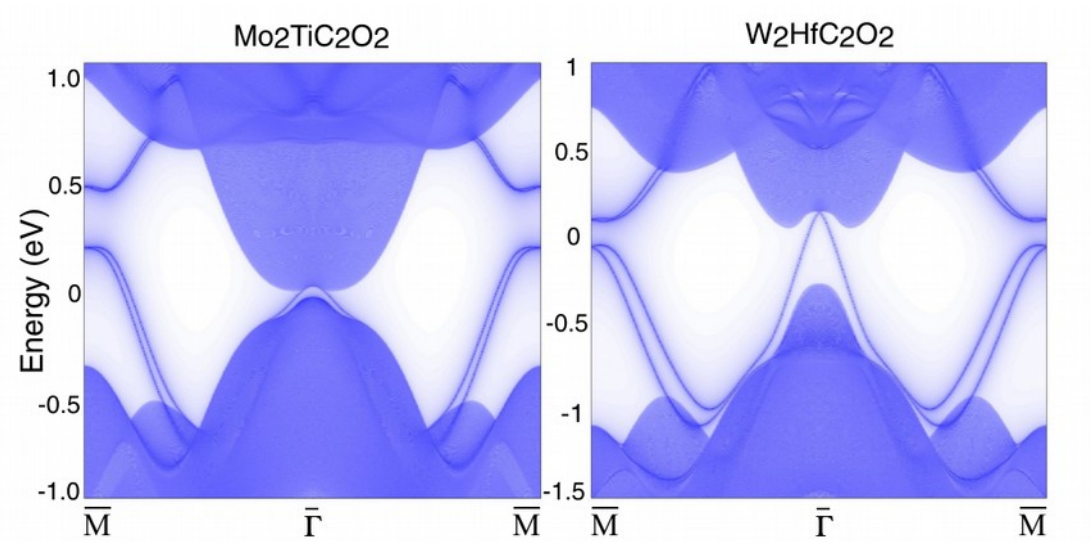
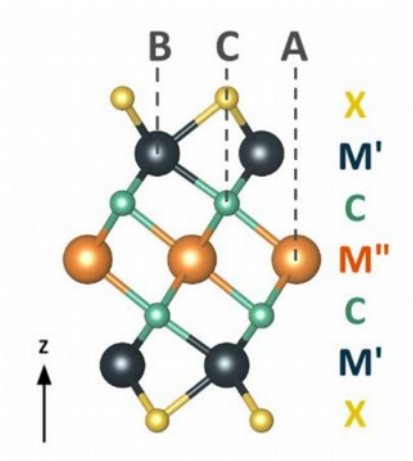


FIG. 4. Edge band structures for $Mo_2TiC_2O_2$ and $W_2HfC_2O_2$. The Fermi energy is located at zero energy.

Search

$M'_2M''C_2X_2$



Yellow X : F,Cl,Br,I, O, or H
Black M' : V, Nb, or Tb
light green : C
orange M” : Ti, Hf, or Zr

Group → 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period ↓																	
1	1 H																2 He
2	3 Li	4 Be										5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	* 72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	* * 104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
			*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			* *	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Computational Method

Package: Vienna Ab initio simulation package (VASP 5.4.4)

Pseudopotential: Projector augmented wave method (PAW)

Exchange-correction: Generalized Gradient Approximation (PBE)

k-point grid: 12x12x1 Gamma-center Monkhorst-Pack

Cut off energy: 400 eV

vacuum space : ~20 Å

forces : < 10^{-3} eV/Å in fully relaxed structures

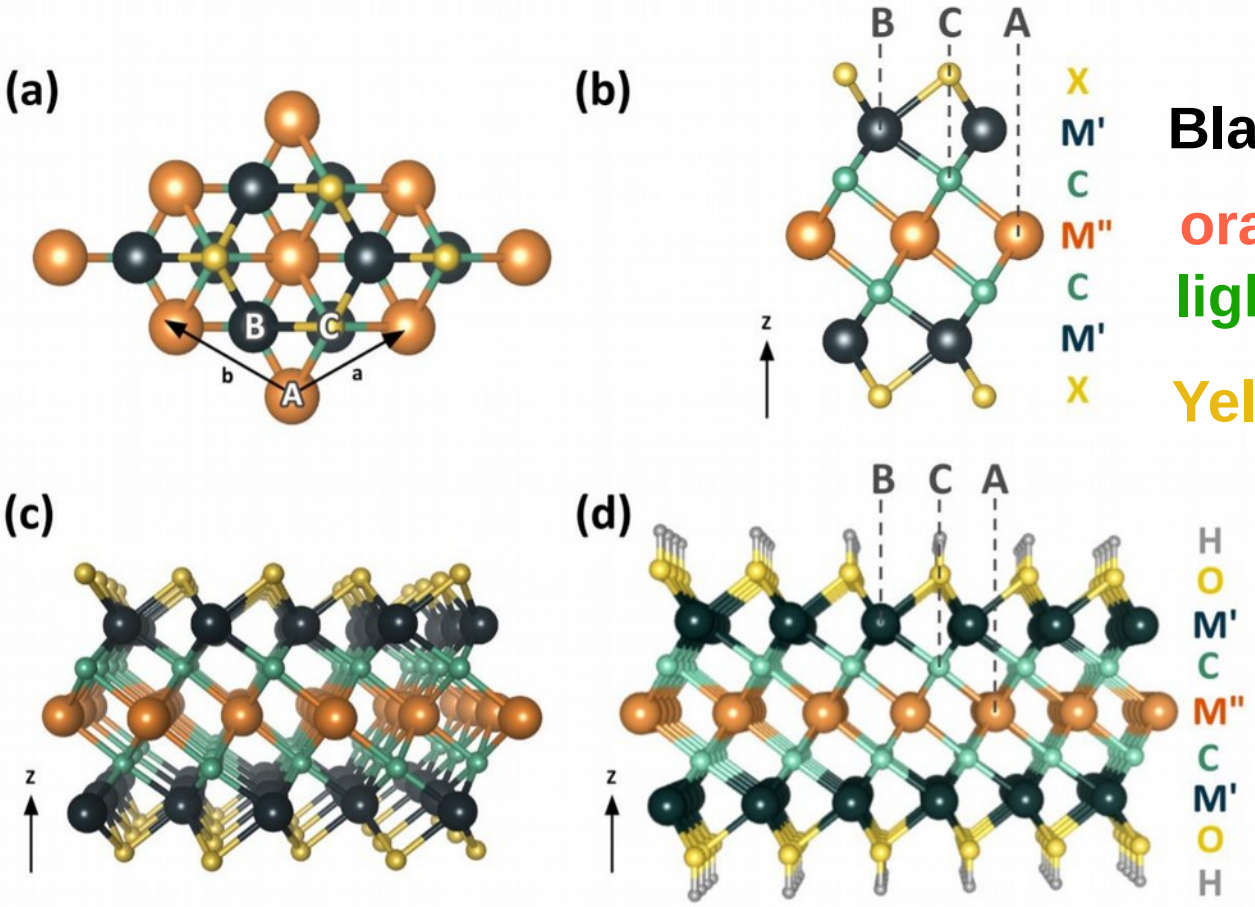
convergence criteria : 10^{-6}eV

Crystal structure of $M'_2M''C_2X_2$

$M'_2M''C_2X_2$

Top view

Side view



Black M' : V, Nb, or Tb

orange M” : Ti, Hf, or Zr

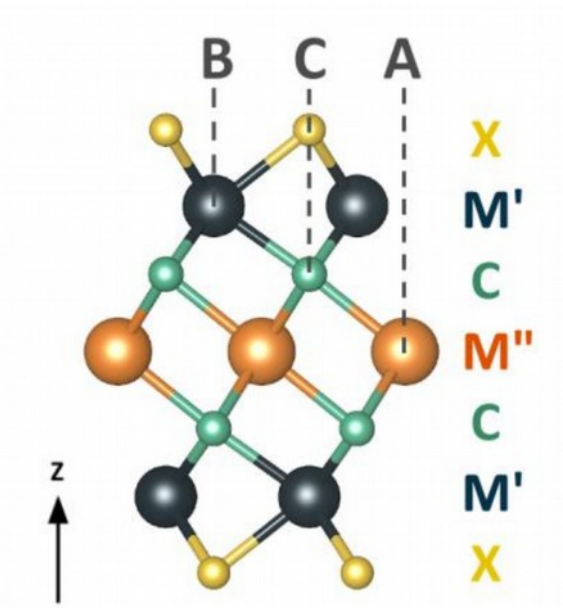
light green : C

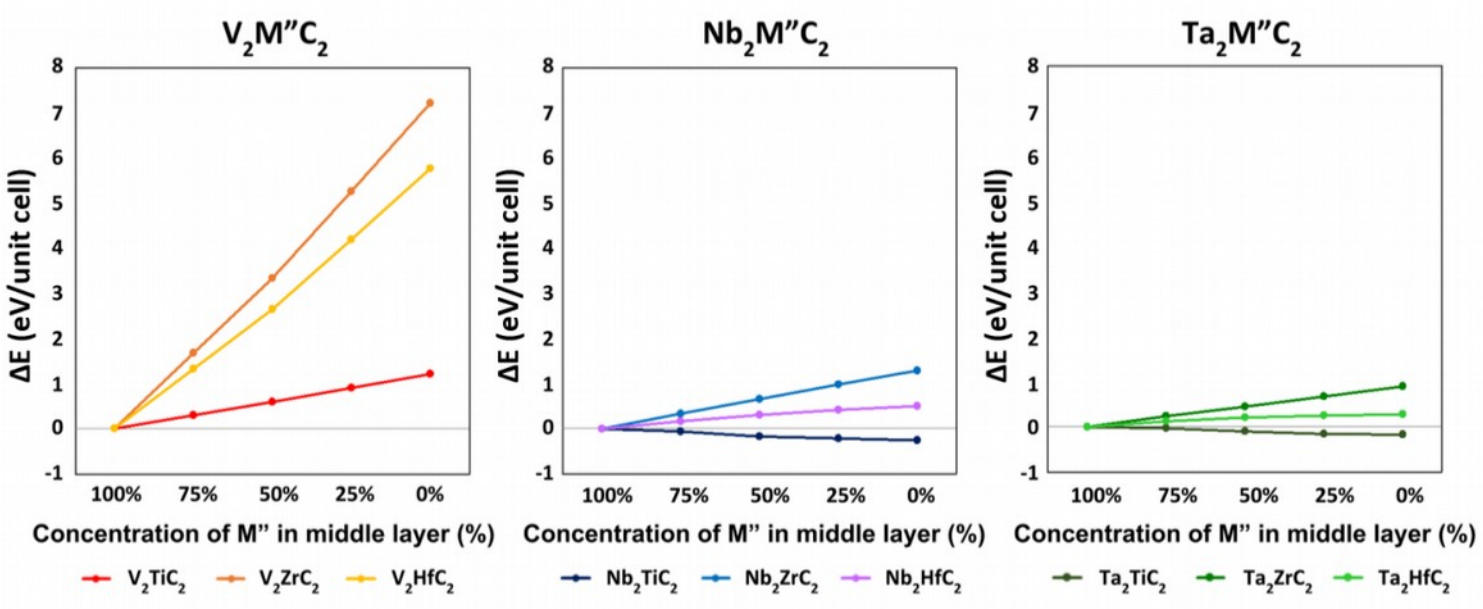
Yellow X : F,Cl,Br,I, O, H, OH

$M'_2M''C_2F_2$

$M'_2M''C_2(OH)_2$

Order Double Transition Metals MXenes





The 100% concentration of M'' in the middle layer corresponds to the fully ordered structure.

Most of them are order, except Nb_2TiC_2 and Ta_2TiC_2.

$V_2TiC_2X_2$ (X=F, Cl, Br, I, O, OH)

	Lattice constant(Å)	Z_2	System band gap (meV)	Γ-point band gap (meV)
$V_2TiC_2F_2$	2.86	1	37	39
$V_2TiC_2Cl_2$	3.02	1	-187	12
$V_2TiC_2Br_2$	3.10	1	-446	135
$V_2TiC_2I_2$	3.24	1	-463	270
$V_2TiC_2O_2$	2.88	0	-788	14
$V_2TiC_2H_2$	2.88	1	-419	29
$V_2TiC_2(OH)_2$	2.84	1	-151	48

Table 1. The lattice constant, Z_2 topological invariant, system band gap, and Γ-point band gap of $V_2TiC_2X_2$ (X = F, Cl, Br, I, O, H, or OH).

$V_2TiC_2X_2$ (where X = F, Cl, I, Br, H, or OH) are topological semimetals, and only $V_2TiC_2O_2$ is a trivial insulator

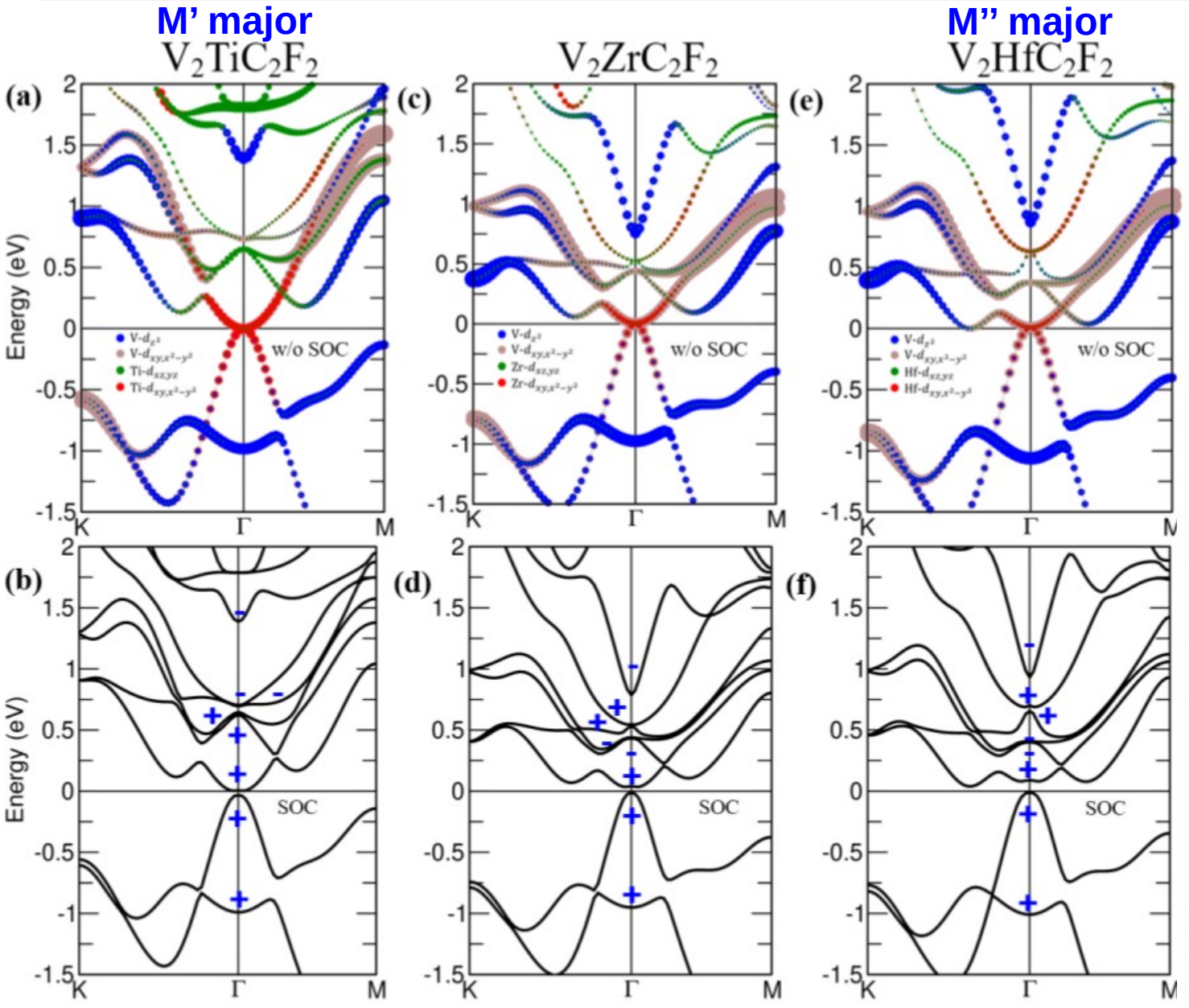
$M'_2M''C_2F_2$ (M'=V,Nb,Ta ; M''=Ti,Zr,Hf)

	Lattice constant (Å)	Z_2	System band gap (meV) PBE(HSE06)	Γ-point band gap (meV) PBE(HSE06)
$V_2TiC_2F_2$	2.86	1	37 (212)	39 (248)
$V_2ZrC_2F_2$	2.99	1	48 (192)	55 (252)
$V_2HfC_2F_2$	2.96	1	49 (295)	101 (389)
$Nb_2TiC_2F_2$	3.00	1	53 (223)	82 (259)
$Nb_2ZrC_2F_2$	3.07	1	4 (139)	110 (263)
$Nb_2HfC_2F_2$	3.04	1	-6 (130)	217 (399)
$Ta_2TiC_2F_2$	3.01	1	5 (319)	207 (483)
$Ta_2ZrC_2F_2$	3.04	1	-70 (49)	278 (489)
$Ta_2HfC_2F_2$	3.05	1	-23 (128)	424 (658)

Table 2. The lattice constant, Z_2 topological invariant, system band gap, and Γ-point band gap by PBE and HSE06 of $M'_2M''C_2F_2$ (M' = V, Nb, or Ta ; M'' = Ti, Zr, or Hf). The values in the parentheses are obtained by hybrid functional calculations.

Since PBE will underestimate the band gap, HSE06 will give a more accurate band gap. The topological phase is the same in PBE and HSE06 calculations.

Band structures



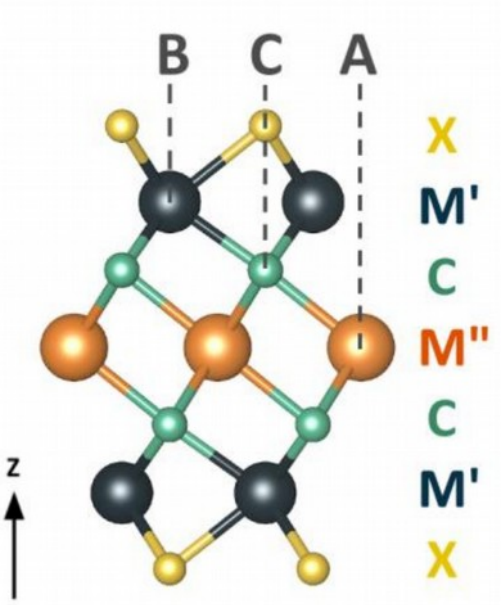
brown M' : V $d_{xy}+d_{x2-y2}$

red M'': Ti $d_{xy}+d_{x2-y2}$

At Γ gap

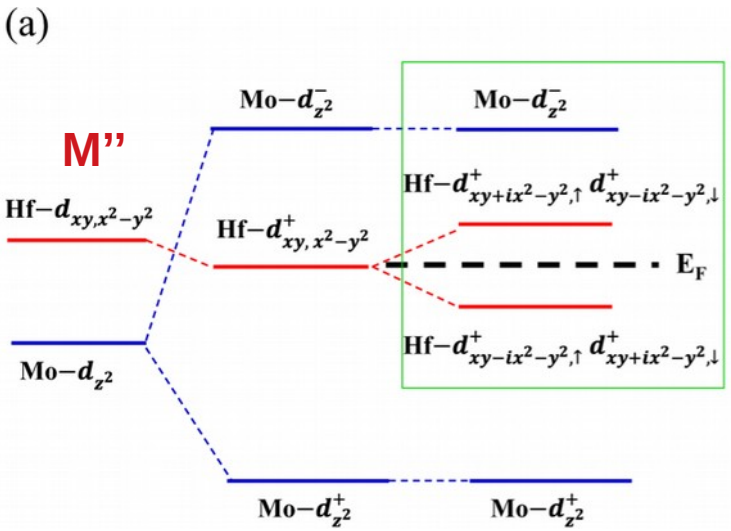
$V_2TiC_2F_2$: Ti $d_{xy}+d_{x2-y2}$

$V_2HfC_2F_2$: V $d_{xy}+d_{x2-y2}$

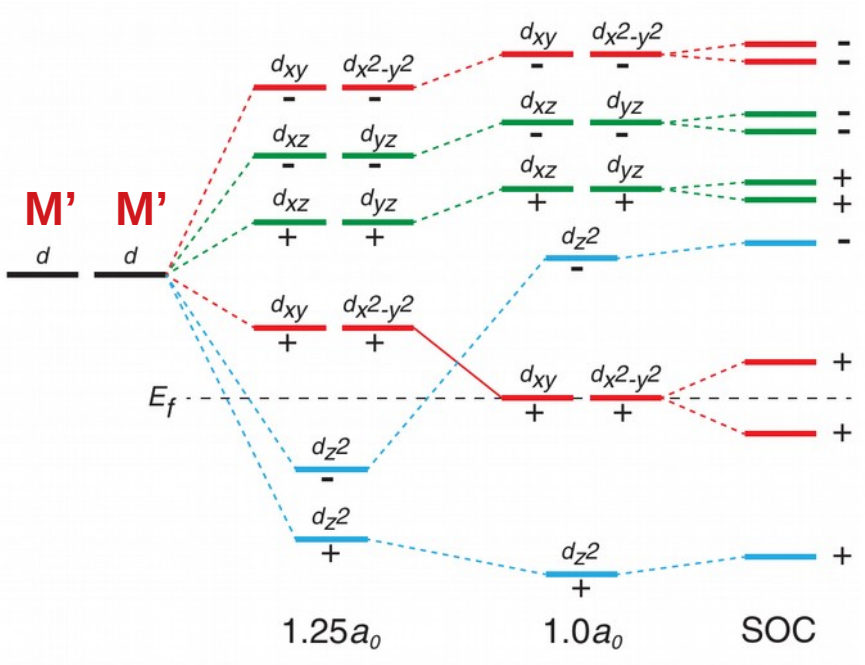


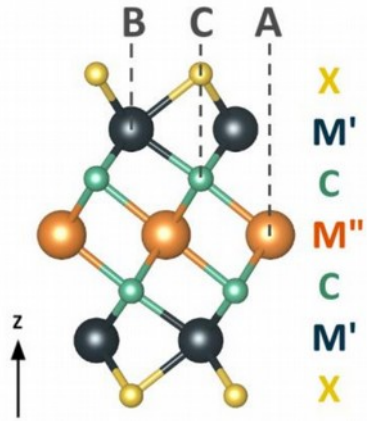
Different mechanism at Γ point

$Mo_2M''C_2O_2$ (M''=Ti,Zr,Hf)



$M'_2M''C_2O_2$ (M'=Mo,W ; M''=Ti,Zr,Hf)





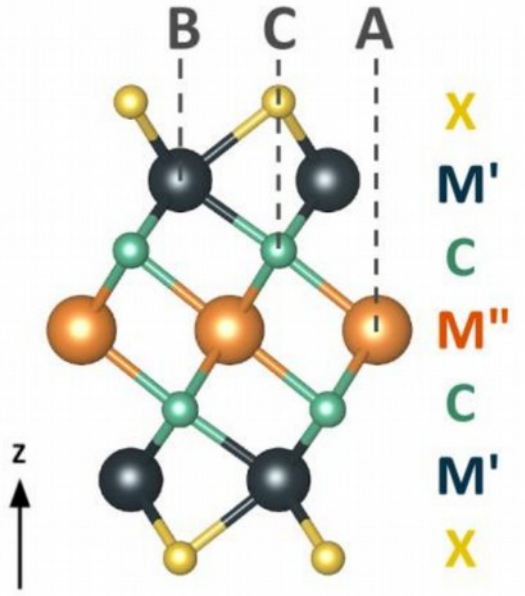
C. Si, K.-H. Jin, J. Zhou, Z. Sun, and F. Liu, Nano Lett. 16, 6584 (2016).

M. Khazaei, A. Ranjbar, M. Arai, and S. Yunoki, Phys. Rev. B 94, 125152 (2016).

Band gaps at the Γ point

$M'_2M''C_2F_2$	SOC gap (eV) at Γ			$d_{xy} + d_{x^2-y^2}$ orbitals at Γ	
	M'&M''	M'	M''	Contribution from M'	Contribution from M''
$V_2TiC_2F_2$	0.0393	0.0245	0.0120	0.231	0.367
$V_2ZrC_2F_2$	0.0553	0.0258	0.0254	0.258	0.232
$V_2HfC_2F_2$	0.1014	0.0203	0.0753	0.244	0.174
$Nb_2TiC_2F_2$	0.0821	0.0654	0.0141	0.182	0.400
$Nb_2ZrC_2F_2$	0.1104	0.0691	0.0372	0.196	0.309
$Nb_2HfC_2F_2$	0.2167	0.0692	0.1416	0.201	0.298
$Ta_2TiC_2F_2$	0.2070	0.1871	0.0163	0.142	0.462
$Ta_2ZrC_2F_2$	0.2777	0.2268	0.0458	0.173	0.369
$Ta_2HfC_2F_2$	0.4237	0.2513	0.1613	0.190	0.334

Gap induced by M' and M''



Band gaps at the Γ point

$M'_2M''C_2F_2$	SOC gap (eV) at Γ			$d_{xy} + d_{x^2-y^2}$ orbitals at Γ	
	M'&M"	M'	M''	Contribution from M'	Contribution from M''
$V_2TiC_2F_2$	0.0393	0.0245	0.0120	0.231	0.367
$V_2ZrC_2F_2$	0.0553	0.0258	0.0254	0.258	0.232
$V_2HfC_2F_2$	0.1014	0.0203	0.0753	0.244	0.174
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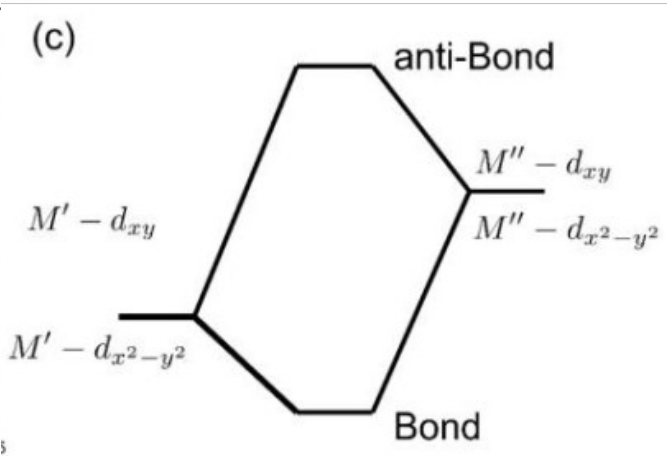
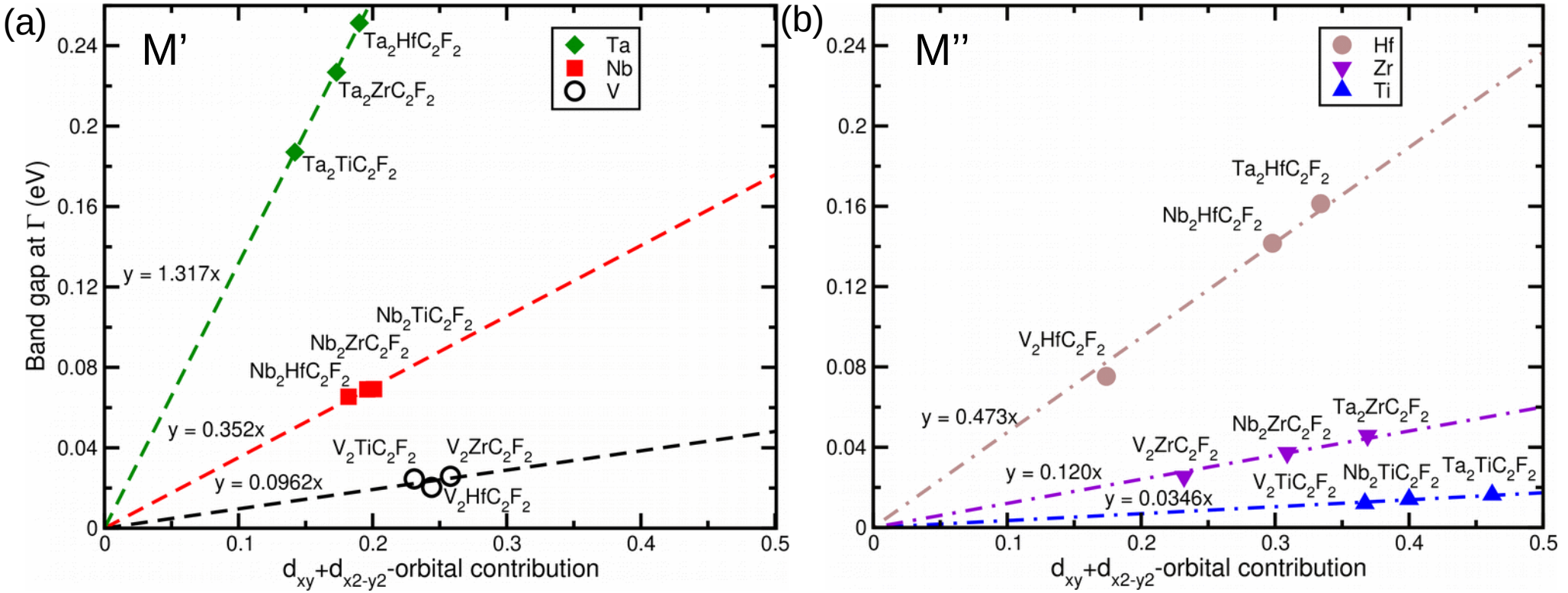
$Ta_2HfC_2F_2$	0.4237	0.2513	0.1613	0.190	0.334



Band gaps at the Γ point

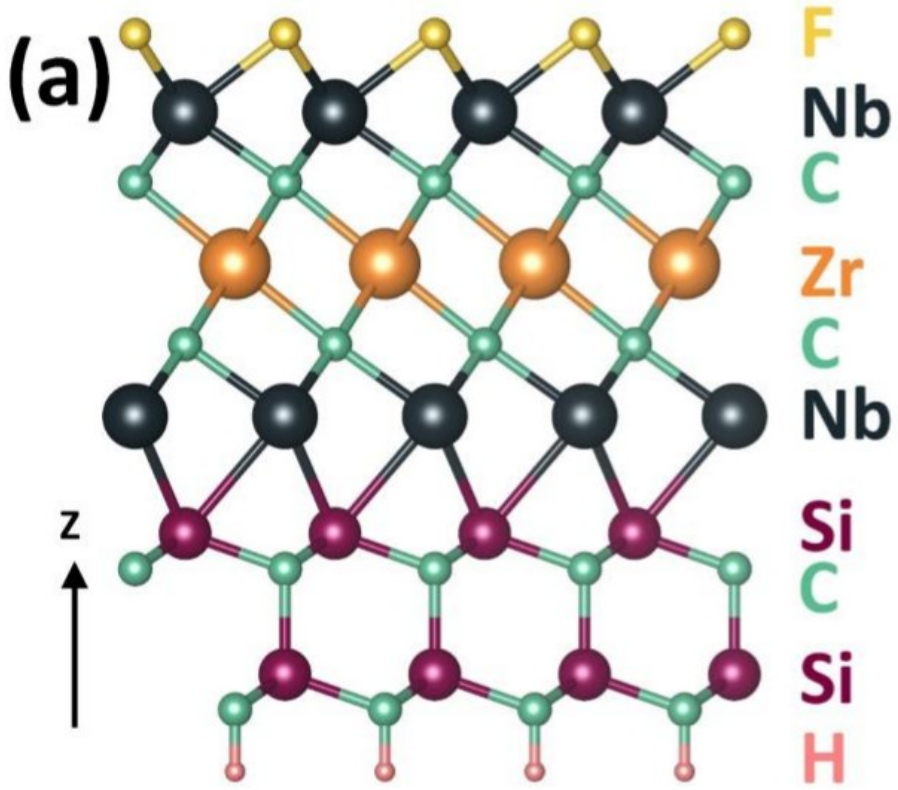


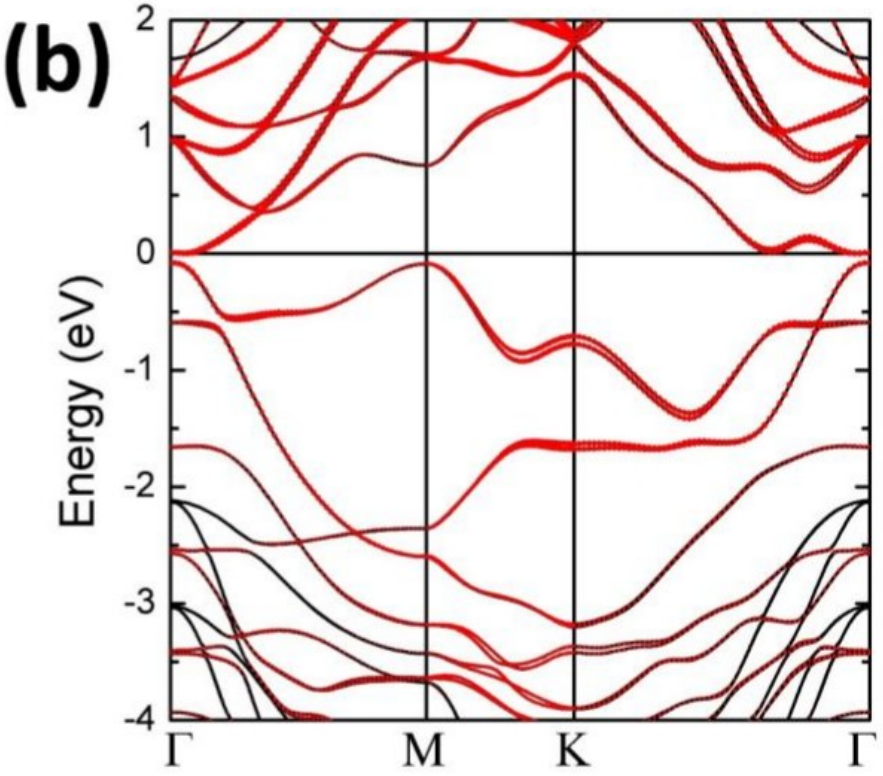
linear combination

$$Gap \sim \langle d_{M'}|\Psi\rangle^2 \lambda_{\mathrm{SOC}}(M') + \langle d_{M''}|\Psi\rangle^2 \lambda_{\mathrm{SOC}}(M'')$$

The substrate supported MXenes

SiC(0001)-supported Nb2ZrC2F2





Red dots : the contribution from Nb and Zr atoms

Conclusions

- Some ordered double-transition metal MXenes, $M'_2M''C_2X_2$ (M' = V, Nb, or Ta; M''= Ti, Zr, or Hf ; X = F, Cl, Br, I, H, or OH) are topological insulators by first-principles calculation.

- Atomic and orbital contribution analyses show that majority of the contribution in the bands near fermi level at the Γ-point are from dxy and dx_2-y_2 orbitals of the transition metal M’ and M’’.

- Propose SiC(0001) as a candidate substrate for material realization